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Computer simulation of defect clusters in UO_2 and their dependence on composition

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HIGHLIGHTS

- Edge-sharing 2:2:2 Willis cluster chains most stable defects in $UO_{2.125}$ and $UO_{2.25}$.
- Unstable relative to split di-interstitial cluster at $UO_{2.0625}$.
- More stable than competing defects (cuboctahedra/split-interstitials) at $UO_{2.125}$.
- U^{5+} predicted as charge compensating species.
- Defect behaviour dictated by stoichiometry/composition.

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ABSTRACT

It is recognised that point defects play a key role in the behaviour and properties of many technologically significant oxides. What is less well understood is how these defects cluster together and, crucially, the extent to which the clusters change with composition. We chose to investigate this phenomenon by considering UO_2, a nuclear fuel material for which there is contradictory data in the literature concerning defect clustering as a function of oxygen content. Early studies of fluorite UO_{2+x} proposed a model based on 2:2:2 Willis clusters whilst more recent research suggests cuboctahedral or split quad-interstitial defect clustering. Here we use the PBE + U functional to simulate defective UO_{2+x} and find for $0.125 < x < 0.25$, chains of edge-sharing 2:2:2 Willis clusters to be most stable. Below $x = 0.125$ these chains destabilise, transforming in to split di-interstitial clusters, demonstrating that the type of oxygen cluster present is dependent on local environment and stoichiometry.

1. Introduction

UO_2 is one of the most important materials in the nuclear fuel cycle, forming the primary fuel component in most nuclear reactors worldwide. Although it adopts the fluorite structure it is easily oxidised, particularly under reactor operating conditions, and exhibits complex anion defect behaviour. An intricate knowledge of the properties of hyperstoichiometric UO_2 and the impact of excess oxygen on the materials stability and performance are crucial. As such oxygen defects in UO_2 are a well-known phenomenon that has been the subject of considerable experimental [1–5] and computational research [6–12].

The first hyperstoichiometric UO_2 model was derived from the neutron diffraction measurements of Willis [1–3] that suggested oxygen interstitials (O_i) do not occupy the octahedral site at the centre of oxygen sub-lattice cubes but rather occupy two positions displaced approximately 1 Å from the octahedral site along ⟨1 1 0⟩ and ⟨1 1 1⟩ directions, designated O′ and O″, respectively (Fig. 1(a)). These findings led Willis to propose a clustering model under which these O_i aggregate, now referred to as Willis clusters [13]. The foremost of these complexes is the 2:2:2 cluster, named for the combination of two O′ interstitials, two O vacancies (V_O) and two O″ interstitials. Periodic chains of isolated 2:2:2 clusters were later used to rationalise the structures of the fluorite based uranium oxides U_4O_9 and U_3O_7 (both defective fluorite-based materials) by Allen et al. [4,5]. The more recent study of Bevan et al. [14] proposed the cuboctahedral cluster (COT-12) as a structural feature of U_4O_9. This cluster is formed of eight V_O (a vacant oxygen sub-lattice cube) replaced by 12 O_i (in a cuboctahedron) (Fig. 1(c)). This result was supported by the work of Desgranges et al. [15], and has subsequently been considered as a defect arrangement in UO_{2+x}. Most recently He et al. reported the COT-12 cluster to dominate in U_4O_9, whilst 2:2:2 Willis clusters

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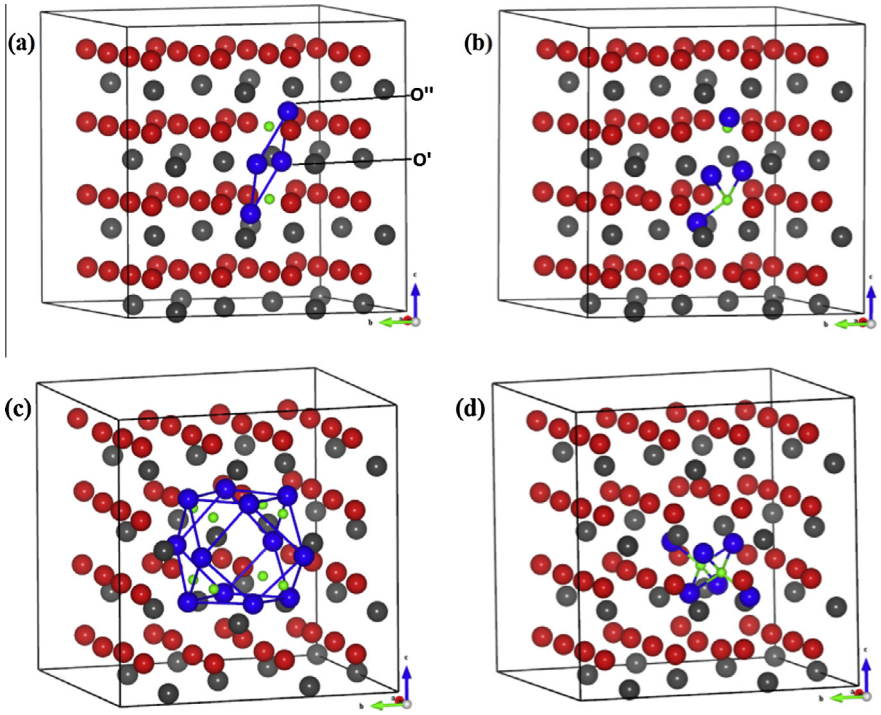

Fig. 1. Relaxation of a 2:2:2 Willis cluster (a) to a split di-interstitial cluster (b), (c) shows a 12 atom cuboctahedral cluster and (d) is a split quad-interstitial cluster. Black spheres represent U ions, red indicate fluorite O ions, blue designate O_i and green represent V_O. Bonds have been drawn in (a) and (c) between O_i and in (b) and (d) between O_i and V_O to highlight the cluster geometries. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and point interstitials form at lower stoichiometries ($UO_{2.15-2.3}$ and $UO_{2.00-2.05}$) [16].

The early theoretical work of Catlow assessed a number of Willis type clusters and found them all to be stable using potential-based methods [6]. More recently "split interstitial" type clusters (Fig. 1) have emerged from computational studies as stable species following the potential based investigation of Govers et al. which found the 2:2:2 cluster in a UO_2 supercell relaxed to a split di-interstitial [13] (Fig. 1(b)); a single V_O with three O_i displaced approximately 1.6 Å in ⟨1 1 1⟩ directions from the V_O. This result was later confirmed by the LSDA + U calculations of Geng et al. [7]. The family of split interstitial clusters was extended to include tri-interstitials [8] (a di-interstitial with the fourth O_i site occupied) and quad-interstitials [9] (two di-interstitials on adjacent sites, giving a total of two V_O and six O_i) (Fig. 1(d)). Following this Andersson et al. postulated a model for U_4O_9 based on a UO_2 supercell containing multiple split quad-interstitial clusters; following the prediction of their LSDA + U calculations that the quad-interstitial is more stable than its cuboctahedral counterpart [12].

Thus despite renewed interest in UO_{2+x}, U_4O_9 and U_3O_7 there is still considerable debate over their structures. Experimentally this is due in no small part to the difficulty in distinguishing defect signals from supercell-related peaks whilst computationally the unit cells can be prohibitively large to simulate with DFT [12].

Here we present our recent simulations, including U_4O_9 stoichiometry phases based on defective UO_2 supercells. Starting from a 48 atom UO_2 supercell ($1 \times 2 \times 2$) we examine all 33 symmetry inequivalent arrangements of four O_i and all 11 unique

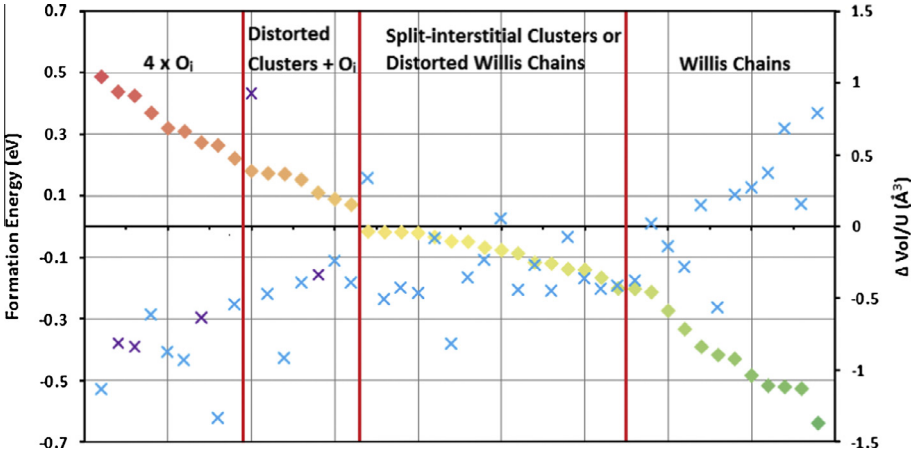

Fig. 2. Plot showing predicted formation energies for each calculated U_4O_9 phase (diamonds) and change in volume relative to UO_2 per uranium ion (crosses). Purple markers indicate one or more U(VI) ions were predicted for that system. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Predicted formation energies for selected U_4O_9 phases, $UO_{2.125}$ and $UO_{2.0625}$. Additional systems are included for comparison. COT-12 is a 12 atom cuboctahedral cluster, di is a split di-interstitial cluster and quad is a split quad-interstitial cluster.

Stoich	Figs.	Config	$E_{Formation}$ (eV)	Δ Vol (%)
$UO_{2.25}$	3(d)	$4 \times O_i$	0.49	−1.14
$UO_{2.25}$	3(c)	$2{:}2{:}2/2 \times O_i$	0.18	0.93
$UO_{2.25}$	3(a)	2:2:2 chain	−0.52	0.68
$UO_{2.25}$	3(b)	2:2:2 chain	−0.53	0.16
$UO_{2.125}$	3(a) + UO_2 bulk	2:2:2 chain	−0.68	0.32
$UO_{2.125}$	1(c)	COT-12	−0.52	0.32
$UO_{2.125}$	1(d)	quad	−0.55	−0.53
$UO_{2.0625}$	1(b)	di	−0.97	0.14

configurations of two di-interstitial clusters, both having U_4O_9 stoichiometry. Then the most stable configuration from these simulations is placed in a $2 \times 2 \times 2$ UO_2 supercell (96 atoms) to produce $UO_{2.125}$ and $UO_{2.0625}$ systems, allowing us to examine a greater range of stoichiometries and how overall phase composition affects defect cluster stability.

2. Methodology

All calculations were performed using PAW pseudo-potentials and the GGA in VASP [17] with the PBE + U functional [18]. The Dudarev scheme [19] ($U = 4.5$ eV, $J = 0.54$ eV [20]) and a plane-wave cutoff energy of 400 eV were employed. $4 \times 2 \times 2$ k-point meshes were used for U_4O_9 (48 atoms) and $2 \times 2 \times 2$ grids for $UO_{2.125/2.0625}$ systems (96 atoms). These cutoff and k-point settings are in accordance with previous DFT studies [7,9]. Convergence criteria for electronic and ionic relaxation schemes were 1×10^{-6} eV/atom and 0.01 eV/Å respectively. This methodology is consistent with previous studies of defects in UO_2 [8,9]. Symmetry inequivalent defect configurations were identified using the site-occupancy disorder (SOD) program [21] and all calculations used $1k$ antiferromagnetic (AFM) ordering, considered to be an appropriate approximation for the experimentally observed $3k$ noncollinear AFM ordering [22,23].

The formation energies of the defective phases relative to UO_2 were calculated by subtracting the predicted oxygen chemical potential (−4.93 eV/O ca. exp. −5.1 eV/O [24]) from the VASP calculated total energy, in accordance with comparable studies in the literature [8,9,12]. All formation energies are expressed per excess O_i introduced.

3. Results and Discussion

The U_4O_9 simulation results predict a number of different defect configurations over a wide range of stability with some common characteristics amongst the most and least stable systems. Fig. 2 is a plot of formation energy and volume change for each U_4O_9 system. Table 1 shows formation energies and defect configurations of selected simulations. Stability is related to the amount of O_i bound in clusters compared to the amount of isolated O_i (Fig. 2). We found that a single 2:2:2 Willis cluster ($UO_{2.0625}$) relaxes to a split di-interstitial cluster, as reported by Govers et al. [13], Geng et al. [7], Andersson et al. [25] and Wang et al. [26]. However, we found that the most stable U_4O_9 configurations contain a single or double chain of 2:2:2 Willis clusters suggesting only groups of Willis clusters are stable at particular local stoichiometries. Wang et al. report the O′/O″ ratio is consistent with Willis clusters at $UO_{2.11\text{-}2.13}$ stoichiometry, however split-interstitial type clusters dominate the UO_{2+x} region with the Willis cluster representing a transition state

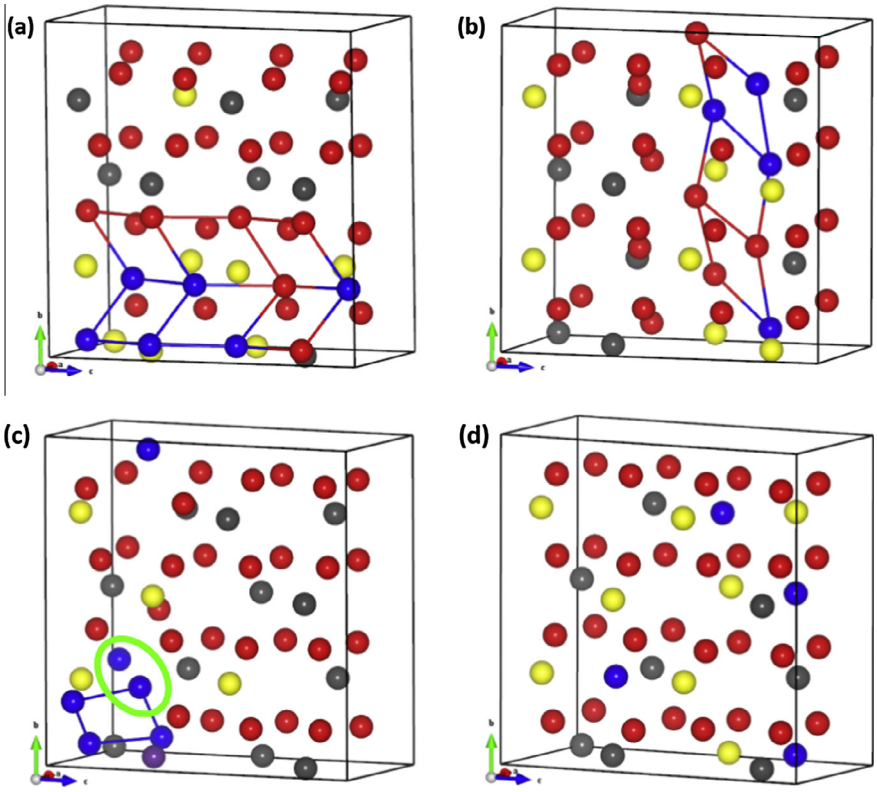

Fig. 3. Relaxed U_4O_9 phases (a) a double 2:2:2 Willis cluster chain, (b) a single 2:2:2 Willis cluster chain, (c) a single distorted 2:2:2 Willis cluster and (d) four isolated O_i. Colour is the same as Fig. 1 with the addition of yellow and purple spheres to represent U (V) and U (VI) ions respectively. To highlight the 2:2:2 clusters bonds have been drawn between their constituent oxygen ions. The "peroxide" O_i have been circled in (c). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

[26]. Of the 44 U_4O_9 systems almost half relaxed to a configuration involving edge-sharing 2:2:2 cluster chains (most stable), a quarter relaxed to four isolated O_i (least stable) and the remainder to combinations of split interstitial clusters and isolated O_i (intermediate stability). Distorted 2:2:2 Willis cluster chains were less stable than undistorted; the distorted chains being comparable in stability to undistorted split-interstitial based systems. The stable, undistorted 2:2:2 cluster chains all align in ⟨100⟩ directions linked by edge-sharing (Fig. 3), similarly to the chains reported by Allen et al. [5].

There is moderate correlation ($r = 0.63$) between U_4O_9 stability and volume change relative to UO_2; the least stable systems generally show a volume decrease whilst the most stable increase. Consequently with applied pressure we would predict Willis chains to destabilise and O_i to become the favoured defect arrangement.

Once 2:2:2 Willis cluster chains were identified as stable entities at the U_4O_9 stoichiometry we sought to isolate chains (and individual clusters) at lower oxygen stoichiometries by generating $2 \times 2 \times 2$ UO_2 supercells with stoichiometries of $UO_{2.125}$ and $UO_{2.0625}$. In the $UO_{2.125}$ simulation the chains retained their geometry and were still predicted to be a stable defect arrangement. This is in accordance with Willis' initial observations of the cluster from $UO_{2.13}$ stoichiometry up [1]. The arrangement was almost identical to that found in the U_4O_9 structure, retaining the cluster chains, implying these are necessary to stabilise the cluster. To lower the stoichiometry to $UO_{2.0625}$ we removed two oxygen ions from the $UO_{2.125}$ cell (breaking the cluster chain to give only two edge-sharing 2:2:2 clusters). This is in fact the minimum stoichiometry (in a $2 \times 2 \times 2$ UO_2 supercell) possible to create a 2:2:2 cluster as it contains only two O_i, however the system relaxed to a split di-interstitial cluster, as previously reported [7,13,25]. The formation energies of these defects are in Table 1 and the Willis-based $UO_{2.125}$ systems are found to be more stable than the equivalent cuboctahedral and split quad-interstitial containing cells (Fig. 1(c) and (d)).

Stability of the U_4O_9 phases is also related to the species that compensate the additional charge introduced by O_i. In all simulations this is oxidation of U (IV); the vast majority of which is to U (V) however in five of the least stable configurations ($E_{form} = 0.11$–0.44 eV) one or two U (VI) ions are also predicted. Fig. 2 highlights which systems contain U (VI) and Fig. 3 shows the distribution of U (V) and (VI) in four different systems. Where there are cluster chains oxidised uranium ions tend to be in close proximity (Fig. 3(a) and (b)). One of the U (VI) containing phases also features a single distorted 2:2:2 cluster with an adjacent O_i (Fig. 3(c)). We have attributed the low stability of this configuration to the presence of an O_i only 1.443 Å from a 2:2:2 cluster O_i, preventing formation of a chain by distorting the local oxygen sub-lattice. This short O-O bond is indicative of a peroxide ion (O_2^{2-}), previously predicted by Andersson et al. in their DFT study of UO_2 oxidation[12]. The prediction of U_4O_9 containing only U (IV) and U (V) ions is supported by the experiments of Kvashnina et al. who reached the same conclusion using x-ray absorption near edge structure (XANES) spectroscopy [27].

The coordination at U (V) and U (VI) sites adjoining 2:2:2 clusters (Fig. 4) both differ significantly from the parent fluorite lattice. U (V) sites retain a coordination number of eight but the 2:2:2 cluster significantly distorts their coordination sphere and slightly lowers the average U–O bond length to 2.294 Å from 2.368 Å. Observing Fig. 4(a) the four in-plane oxygen ions on the left show half of an oxygen sub-lattice cube (aligned in the (011) plane) whilst the other four form a flattened tetrahedron. At U (VI) sites a larger local distortion to the oxygen sub-lattice results in further reduction of the average U–O bond length to 2.188 Å and the emergence of two shorter, collinear "uranyl" type bonds (Fig. 4(b)). The coordination is a puckered pentagonal bipyramid and when considered with the non-symmetrical uranyl-type bonds the U (VI) site

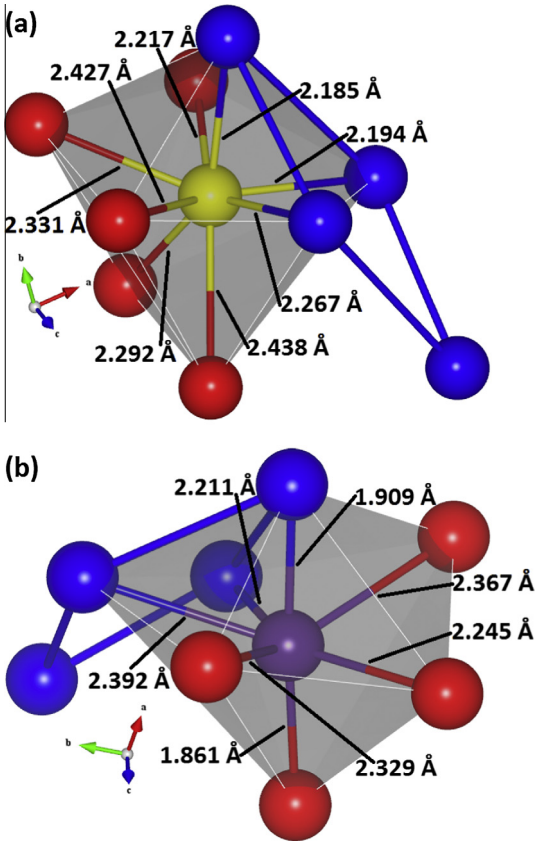

Fig. 4. Coordination of U (V) (a) and U (VI) (b) ions neighbouring 2:2:2 clusters. Colour is the same as Figs. 1 and 2. To highlight the 2:2:2 clusters bonds have been drawn between their constituent oxygen ions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

is strongly reminiscent of the η-UO_3 polymorph which also contains these structural features [28,29]. The prediction that U (VI) is unstable in U_4O_9 systems demonstrates the preference of U (VI) ions for layered-type structures (e.g. U_3O_8 and UO_3) [27].

We have also computed the electronic band gaps for each phase discussed here, finding the most stable U_4O_9 systems (i.e. those containing 2:2:2 cluster chains) to have band gaps between 1.48 and 1.61 eV. The $UO_{2.125}$ system was found to have a lower band gap of 1.38 eV and $UO_{2.0625}$ lower again at 1.29 eV. Although no experimental measurements of the U_4O_9 band gaps could be found our result compares favourably with the LSDA + U calculated value of 1.68 eV from He et al. [30]. Given the paucity of data available in this area further investigation is warranted before we can draw any conclusions.

4. Conclusions

In summary, we investigated defective fluorite supercells with a range of stoichiometries and found for U_4O_9 and $UO_{2.125}$ there are stable configurations of edge-sharing 2:2:2 Willis cluster chains. Reducing the stoichiometry to $UO_{2.125}$ we find that these chains are retained as the defect cluster remains present in accordance with the original observations of Willis. Further reduction of the stoichiometry to $UO_{2.0625}$ (a single 2:2:2 Willis cluster or two edge-sharing ones in a $2 \times 2 \times 2$ UO_2 supercell) leads to formation of a split di-interstitial cluster in line with previous calculations. Therefore we propose that the 2:2:2 Willis cluster is a genuine feature of UO_{2+x} but its formation is dependent on oxygen content and

it is only stabilised in edge-sharing chains, as reported by Allen et al. [5]. U(V) ions are predicted as charge compensating species for the oxygen defects, supporting observations that (VI) is not a stable oxidation state for U in U_4O_9. Having identified the oxygen concentration dependence of defects over $UO_{2\cdot0625-2.25}$ it would be pertinent to extend the investigation to a broader range of stoichiometries; and indeed examine the extent to which defect cluster formation is dependent on oxygen stoichiometry for other materials that show mixed oxidation states. A suitable extension to this work would be including additional layers of complexity such as alternative magnetic orderings, spin orbit coupling and multiple *f* orbital occupations. Recent studies from Dorado et al. [31] and Allen and Watson [32] have demonstrated that occupational matrix control can be used to locate the global minimum of the system, avoiding the occurrence of metastable states.

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